

## IDENTIFICATION OF ORGANIC COMPOUNDS IN THE BITUMEN OF CHATTANOOGA OIL SHALE

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### ABSTRACT

The bitumen of Chattanooga oil shale has been extracted with benzene. The benzene-soluble material was separated into acid, base and neutral fractions with ion exchange chromatography. This separation scheme has been used extensively to separate the organic material in Green River oil shale. The acid fraction was esterified with  $\text{BF}_3/\text{MeOH}$ . A large portion of the acid fraction was not esterified and this material was considered to be phenolic. The bases were separated into two fractions using alumina. The esters, the two base fractions and the total neutral fraction were analyzed using gas chromatography coupled to mass spectrometry. Two series constituting the methyl esters of normal carboxylic acids and carboxylic acids containing one double bond were identified. No homologous series were indicated in the base fraction. The base fraction was highly aliphatic. The major components in the neutral fractions were two series constituting normal and isoprenoid alkanes. A series of cycloalkanes and a series of alkenes were also indicated. The analysis scheme employed functions well for the separation and identification of aliphatic materials.

### INTRODUCTION

Several cores of Chattanooga Shale from Tennessee have been extracted with benzene. The benzene-soluble bitumens have been further separated into acid, base and neutral fractions (1). In that study, the bitumen was dissolved in benzene and the acid fraction was absorbed on IRA 904 anion exchange resin. The acids were stripped from the resin by Soxhlet extraction with five percent acetic acid in benzene. In a similar fashion, the bases were absorbed on A-15 cation exchange resin and stripped by Soxhlet extraction with five percent isopropyl amine in benzene. The unabsorbed material constituted the neutral fraction. This separation scheme was adapted from the scheme proposed by Jewell et al. (2) and has been used to separate organic material associated with Green River oil shale (3,4,5). This scheme has been very successful in separating the mostly aliphatic material in Green River oil shale. Chattanooga oil shale, however, has been shown to be highly aromatic (6). The work presented in this paper was performed to identify components of the bitumen of Chattanooga oil shale and to make a comparison of the results to corresponding results for Green River oil shale.

Cooper (7) has extracted a Chattanooga oil shale outcrop in Texas and identified the presence of normal carboxylic acids from  $\text{C}_8$  to  $\text{C}_{28}$  with a maximum at  $\text{C}_{16}$ . The ratio of even numbered carboxylic acids to odd numbered acids was measured at 1.56. Leddy et al. (8) extracted Antrim oil shale (a similar formation of the same age in

Michigan) with toluene and identified a series of normal alkanes and porphyrins.

#### EXPERIMENTAL

The acid fractions were esterified using boron trifluoride in methanol as described by McGowan and Diehl (9). Approximately 0.1-g samples of the acid fraction were boiled for five minutes in five mL of 14 percent boron trifluoride in methanol. The esters were extracted with two five-mL portions of pentane. Not all of the organic material was extracted into pentane. The base fraction was placed on an activated alumina column and eluted with hexane followed by benzene thus producing two fractions. The neutral fraction was not separated further.

The esters, the total base fraction and the neutral fraction were initially separated by gas chromatography on a six-foot, 1/8-in Tenax column which was temperature programmed from 100°C to 350°C with a flame ionization detector (FID). The esters the two base fractions and the neutral fraction were later separated on a 30-meter DB-5 fused silica capillary column which was temperature programmed from 50°C to 310°C with FID detection. Finally the separation was performed using the capillary column coupled to a mass spectrometer. A Finnegan 4000 GC/MS system was used. Mass spectra were recorded for the major peaks in each fraction.

#### RESULTS AND DISCUSSIONS

The pentane-insoluble organic matter remaining after the esterification process represented a highly polar material. This material was considered to be phenolic. However highly polar esters could also have been present. The presence of inorganic salts in the residue and the high volatility of the produced esters made quantitation of this polar material difficult. Attempts were made to quantitate the amount of weak acids (phenols) in the acid fraction by extraction of the carboxylic acids with NaHCO<sub>3</sub> solutions and back extraction after acidification. The extracted<sup>3</sup> materials and residues were very gelatinous and difficult to work with. No conclusive results were obtained. This material was not analyzed further.

The gas chromatograms resulting from the DB-5 column and flame ionization detector for the esters, the hexane-soluble base fraction and the neutral fraction appear in Fig. 1. Three homologous series account for all of the major peaks in the esters of the acid fraction. One of the series was composed of normal alkanes ranging from C<sub>15</sub> to C<sub>40</sub> with a maximum at C<sub>24</sub>. The alkanes were absorbed by the polyvinyl benzene portion of the ion exchange resin and later stripped by the acetic acid/benzene solvent. The major series in the ester fraction was composed of the methyl esters of normal carboxylic acids. Normal saturated carboxylic acids from C<sub>6</sub> to C<sub>26</sub> were identified with a maximum at C<sub>16</sub>. There was a definite predominance of the even numbered carboxylic acids to the odd numbered carboxylic acids. The methyl esters of the even numbered normal acids constituted 36 percent of the fraction while the methyl esters of the odd numbered normal acids constituted only five percent. A second series was composed of the methyl esters of normal carboxylic acids containing one double bond. Unsaturated acids from C<sub>10</sub> to C<sub>20</sub> were identified with a maximum at C<sub>18</sub>. The

position of the double bond was not identified in this study. However, the mass spectrum of the methyl ester of the  $C_{18}$  unsaturated acid was almost a perfect match with the library generated mass spectrum for methyl oleate. Although not as pronounced as for the saturated acids, there was also a definite predominance of the even numbered unsaturated acids to the odd numbered unsaturated acids. The methyl esters of the even numbered unsaturated acids constituted eleven percent of the fraction while the methyl esters of the odd numbered unsaturated acids constituted four percent. Methyl esters of isoprenoid carboxylic acids were not identified. Methyl esters of aromatic carboxylic acids were not identified.

No clear homologous series of bases were identified. No base was unambiguously identified. The mass spectrum of most the components of the base fraction indicated the presence of alkyl amines. Alkyl amines from  $C_{15}$  to  $C_{26}$  containing from zero to three degrees of unsaturation were indicated. Five components had mass spectra which indicated highly aromatic systems. One of these was tentatively identified as a  $C_{18}$  quinoline (10).

The major series in the neutral fraction was composed of normal alkanes ranging from  $C_{12}$  to  $C_{31}$  with a maximum at  $C_{17}$ . A second homologous series was composed of isoprenoid alkanes ranging from  $C_{15}$  to  $C_{25}$  with a maximum at  $C_{19}$ . Both phytane and pristane were identified. Two other homologous series, together equal in concentration to the isoprenoid series, were composed of hydrocarbons containing one degree of unsaturation. The mass spectra of these compounds indicated a series containing rings and a series containing double bonds. A  $C_{18}$  alkane containing a cyclohexyl ring was identified. Cycloalkanes from  $C_{15}$  to  $C_{22}$  were indicated with a maximum at  $C_{18}$ . A  $C_{17}$  alkene was identified. Alkenes from  $C_{13}$  to  $C_{20}$  were indicated with a maximum at  $C_{17}$ . Two other homologous series, in very low concentration, were indicated by the gas chromatograms but were not identified by mass spectrometry. There was no even to odd predominance in either of the alkane series, the cycloalkane series or the alkene series. No aromatic compounds were indicated as major components of the neutral fraction.

The major compounds identified in this study were essentially the same as the major compounds identified in Green River oil shale (11,12,13,14,15). The notable exceptions were the presence of isoprenoid carboxylic acids and dicarboxylic acids in Green River oil shale; and the presence of unsaturated carboxylic acids and alkenes in Chattanooga oil shale. The presence of unsaturated acids and alkenes was unexpected and has not been noted previously for Chattanooga oil shale. Unsaturated essential fatty acids, such as oleic acid, were probably present at the time of deposition of both Chattanooga and Green River oil shale. However the conditions of lithification have apparently destroyed the double bonds in the case of Green River oil shale while preserving the double bonds in the case of Chattanooga oil shale.

The major components identified in each fraction in this study were aliphatic in nature. Only a few aromatic bases were indicated. The infrared spectra of each fraction (1) indicated the presence of aromatic material. The separation scheme employed in this study including the fractionation, derivatization and gas chromatography

did an excellent job of identifying aliphatic material. While this scheme works well in identifying the primarily aliphatic components in Green River oil shale, the scheme falls short in identifying all the major components of Chattanooga oil shale. The aromatic material present in Chattanooga oil shale was not identified. Some of the aromatic material may have been present in the pentane-insoluble portion of the esterified acids. It is possible that the aromatic material in Chattanooga oil shale is present primarily in the kerogen and not in the soluble bitumen. However this seems unlikely.

#### CONCLUSIONS

A series of normal alkanes and a series of normal carboxylic acids have been identified in the acid fraction of the bitumen of Chattanooga oil shale. An unexpected series of normal carboxylic acids containing one double bond has also been identified. There was a definite predominance of even numbered acids to odd numbered acids. The base fraction was primarily aliphatic. A series of normal alkanes, a series of isoprenoid alkanes and a series of cycloalkanes have been identified in the neutral fraction. An unexpected series of alkenes was also identified. The separation scheme employed does not identify any aromatic materials as major components of the bitumen.

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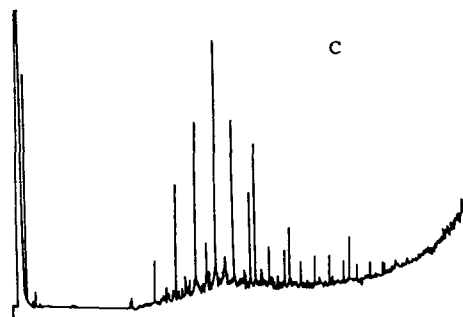
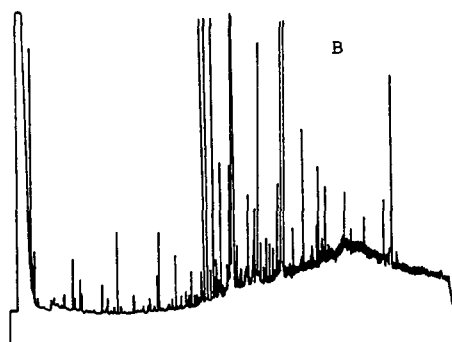
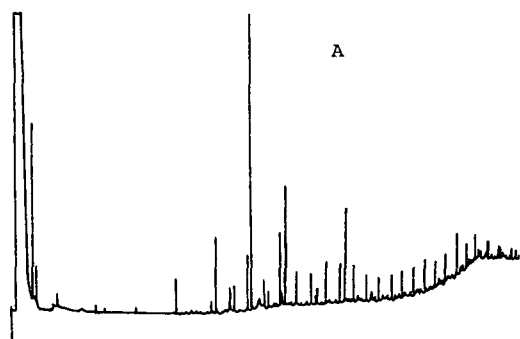


Fig. 1. Gas chromatograms of A. methyl esters of acid fraction B. hexane-soluble fraction C. neutral fraction